Fabrication of superhydrophobic and superoleophilic teflon surfaces using irradiation by nanosecond infrared laser

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Fabrication of superhydrophobic and superoleophilic teflon surfaces using irradiation by nanosecond infrared laser

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Abstract. Polytetrafluoroethylene (PTFE, teflon) possesses excellent stability and low surface energy, which enables its extensive use in the manufacture of biomimetic superhydrophobic surfaces. We proposed a simple and fast method for producing superhydrophobic surfaces by treating the teflon plate by nanosecond pulse infrared irradiation by means of CO_2 laser. The surface relief was visualized by scanning electron microscope. The surface wettability was estimated by measuring the contact angle. The treated teflon superhydrophobic surfaces with static contact angle up to 154°demonstrated self-cleaning properties. The creation of regular two-dimensional structures leading to super-adhesive property of the teflon surface was shown. Thus, it was shown that the surface treating of teflon by nanosecond infrared laser could be used for creation of the super-hydrophobic surfaces for various applications such as self-cleaning, microfluidic devices, and the laboratory-on-chip systems.

1. Introduction

Inspired by nature, superhydrophobic surfaces with a contact angle above 150° have attracted great attention and research efforts in recent years. Lotus leaves and rose petals are two types of superhydrophobic surfaces in nature. Lotus leaves are well-known for the “lotus effect”. These surfaces demonstrate low adhesion to water. The water droplets cannot remain stable on such surfaces, but spontaneously roll off thus removing the usually obtained dust particles from the surfaces [1]. On the other hand, the “petal effect”, being typical for the rose petals, represents a very high adhesion to water resulting in fixation of the water droplets on the surface at any tilted angles [2].

Artificial low-adhesive and high-adhesive superhydrophobic materials find their application in many fields: microfluidics, cell engineering, biosensors, etc. [3,4]. Various technologies have been developed to fabricate such materials. In recent years, laser technologies using picosecond laser [5], femtosecond laser [6], and excimer laser [7] become widely used to prepare superhydrophobic biomimetic materials because of rapid surface micromachining of various patterns with controllable parameters. The femtosecond laser microfabrication has been successfully applied for producing strong non-wetting surfaces because of its negligible heat-affected zone, non-contact process, precise ablation threshold, and high spatial resolution. It has been studied how the irradiation by femtosecond laser can change the surface morphology and wettability of teflon surfaces [8-10].

In this work, we demonstrate that the surface microstructuring of the teflon plates by nanosecond infra-red (IR) laser irradiation leads to essential modification of the wetting characteristics and allows realizing superhydrophobic and superoleophilic properties. It has been shown that the laser treatment increases essentially the initial wetting angle, which allows demonstrating the lotus and rose petal effects and effective self-cleaning.

2. Experimental

2.1. Materials
The study of the polymer surface modification by laser radiation was carried out on 2-mm-thick teflon (fluoroplastic-4) samples. Before irradiation, the samples were cleaned by isopropanol or acetone in an ultrasound bath for 7 min and in deionized water for 5 min. The cleaned samples were dried by compressed dry air. The liquids used for testing of the wetting conditions represent: deionized water, petroleum and mineral aviation oil (MS-8P), and turbine oil (TP-22S).

2.2. Surface treatment
The free-standing platform VersaLASER VLS 3.60 (Universal Laser System, US) equipped with 40 W infrared CO_2 laser source (10.6 μm wavelength) was used. The surface treatment was made with the following parameters: pulse frequency (repetition rate) 450 Hz, scanning speed 270 mm/s, and pulse power 6 W. The size of the spot on the teflon surface after single pulse irradiation was about 100 μm.

The imaging of the surface morphology before and after laser treatment was made by field emission scanning electron microscope (SEM) Merlin (CarlZeiss, Germany) with spatial resolution about 1 nm. The chemical compositions of initial and treated teflon surfaces were measured by X-ray fluorescence spectrometer K-ALPHA (Thermo Fisher Scientific, UK). The contact angle was measured by the lying drop method [4]. A drop of water or oil with a volume of 5 μL was dropped from a height about 5 mm onto a horizontally lying sample at room temperature. The contact angle θ was calculated from the measured droplet sizes:

$$\theta = arccos\frac{(d/2)^2 - h^2}{(d/2)^2 + h^2} \quad (1)$$

where d is the width of the droplet base and h is the droplet height (Fig. 1).

The droplet on the teflon surface was imaged with a digital camera Sony DSC-H9 (Sony Corporation, Japan) with a CCD size of 1 x 2.5 inch. The droplet width and height were measured using the Adobe Illustrator vector graphics editor.

3. Results and discussion

3.1. Initial surface
The surface morphology of the initial teflon surface before laser radiation has been studied by SEM (Fig. 2). It has been shown that it is relatively smooth with irregular graininess and roughness (Ra) about 600 nm measured by optical profilometer WYKO NT 1100 (Veeco, USA). The contact angle for water is about 101°. The well-known teflon hydrophobicity before any treatment can be attributed by the chemical composition only without any significant contribution of the surface topography to the wetting.

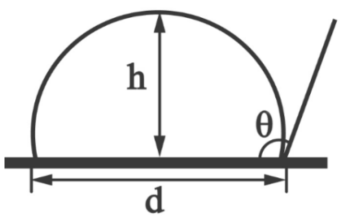

Figure 1. Scheme for measuring the contact angle.

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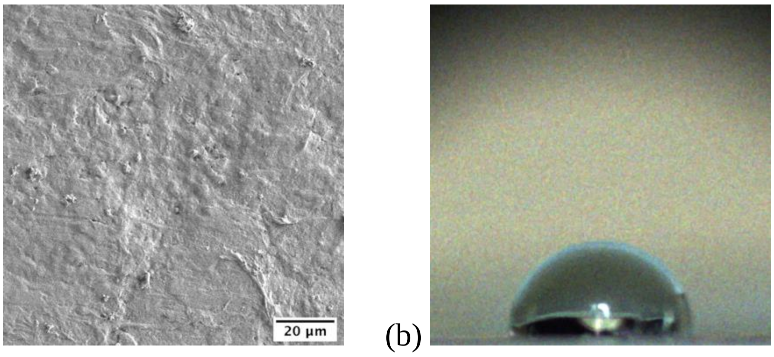
(a) (b)


Figure 2. (a) SEM image of the initial teflon surface, (b) water droplet on it. Droplet volume 5 μL.

3.2. Hydrophobicity of teflon surfaces after laser treatment

The infrared laser treatment of the teflon surface leads to appearance of random intertwined fibrous structure resembling a thick “sponge”. Along with the formation of fibrous teflon in the irradiated zone, polymer destruction occurs with the formation of monomer tetrafluoroethylene [11,12]. Secondary polymerization of teflon leads to the deposition of irregular shaped particles on the polymer fibres with the size range from 20 to 100 nm, which can be assembled into agglomerates (Fig. 3).

The local polymer melting and foaming during laser processing leads to formation of the fibres, which are carried away by the ablation flow. The ablated particles are deposited on the surface along the propagation path. Being in a state of viscous flowing melt, the fibres are fused at the points of contact forming a "spongy" structure.

The contact angle on such a surface is 140.5°. The results of X-ray fluorescence analysis showed that the chemical composition of the polymer was not changed by laser treatment. The obtained increase of hydrophobic properties can be attributed to essential increase of the surface roughness resulting in a decrease of the area of the liquid contact with the surface and increase of the contact angle.

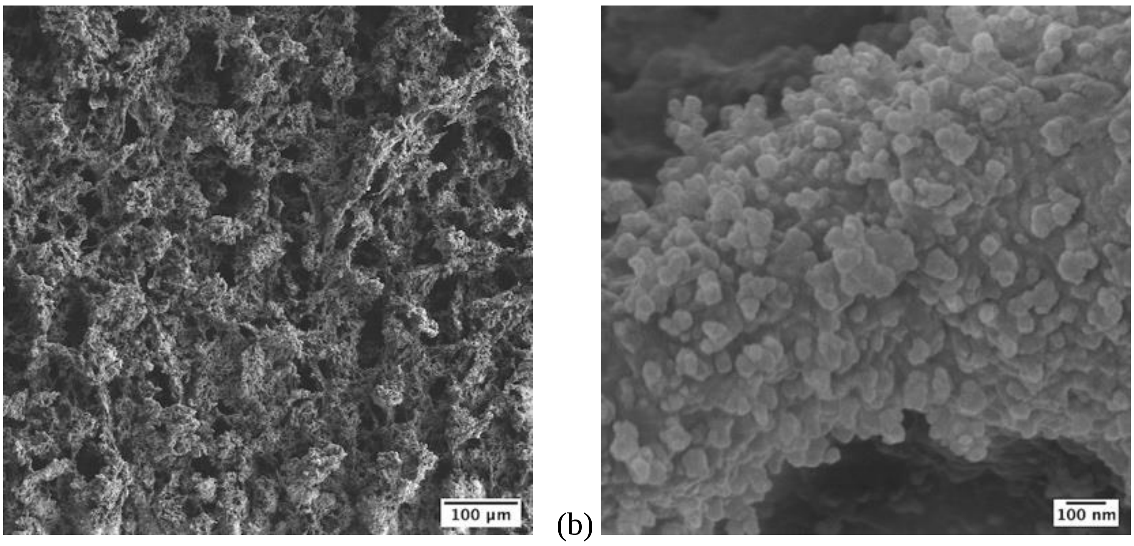
(a) (b)


Figure 3. SEM images of the treated teflon surfaces: (a) the fibrous structure; (b) nanoparticle agglomerates.

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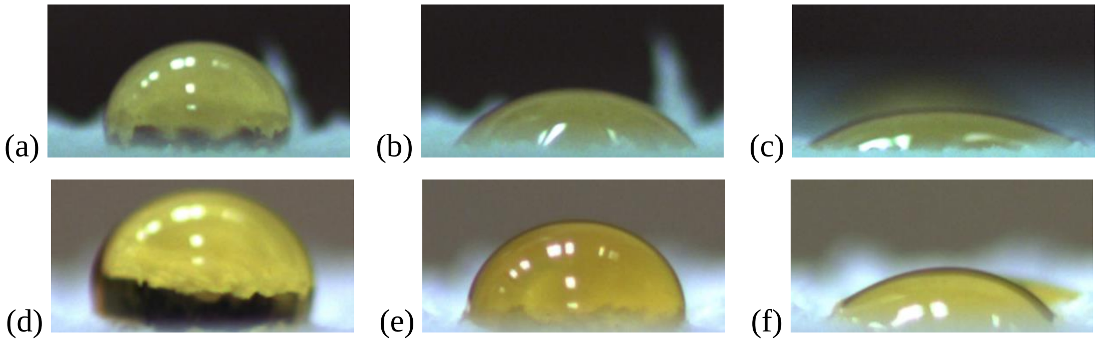

Figure 4. Time evolution of the droplets of (a-c) aviation oil and (d-f) turbine oil on the surface of the modified teflon after: (a, d) 3 min, (b, e) 8 min, and (c, f) 15 min. Droplet volume 5 μL.

3.3. Oleophilicity of teflon surfaces after laser treatment

The wetting of the treated surface by petroleum, turbine and aviation oils was studied. The initial teflon surfaces show strong oleophilicity with contact angle about 15°. The droplets were placed on the surface, and the contact angle was measured after 3, 8, and 15 min.

It was shown that the contact angles of the aviation and turbine oil droplets on the treated teflon surface changed with time (Fig. 4). The oil droplets on the modified teflon surface maintains a spherical shape for 3 min with subsequent decreasing of the contact angle both for aviation (Fig. 4 a-c) and turbine (Fig. 4e-g) oils. Contact angle decreases from 100° to 42° for aviation oil and from 112° to 58° for turbine oil after 15 min demonstrating strong oleophilicity.

It is known that the contact angle change depends on the liquid viscosity and the droplet volume. The observed temporary oleophobicity can be attributed to the high oil viscosity, which affects the rate of oil penetration into existing voids of modified teflon surface.

The oleophilic properties are even more pronounced for petroleum. The contact angle on the initial surface is 18°, while the modified teflon surface exhibits superoleophilic properties with zero contact angle. A petroleum drop placed on the sample spreads over the surface immediately.

The creation of the porous fibrous structures on the teflon surface makes it possible to describe the system under consideration by the Wenzel model [4], according to which the increase of the surface roughness leads to increase of the oleophilic properties up to superoleophilicity observed for the petroleum.

3.4. Self-cleaning surfaces

It is necessary to point out that the described fibrous structures can be easily removed by the mechanical impact. This is the reason to study the effect of the layer thickness of the formed fibres on the wetting effects. The unstable initial fibrous layer with thickness ranged from 420 to 480 μm was mechanically removed from the part of the treated surface (Fig. 5). The thickness of the stable residual layer is about 40 μm. The decrease of the layer thickness leads to noticeable increase of the contact angle. On the surface with initial fibrous layer the contact angle was 134°, while on the residual layer – about 140°.

It was also revealed that the teflon surface modified with IR laser radiation, after removal of the excess fibrous layer, exhibited the pronounced self-cleaning property. For testing, the graphite shavings were placed on the initial and treated teflon plates (Fig. 6). The plates were tilted by 20-30° and water droplets were placed on the surface. On the initial surface, droplets were collected, and water slowly drained from the plate, which led to the formation of spots on

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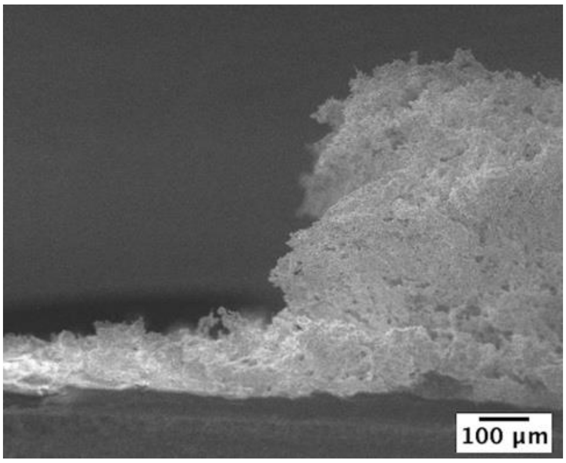

Figure 5. The cross-section of the surface layer of the teflon plate just after laser processing (right) and after mechanical removal of the fibrous layer (left).

the surface. Water droplets placed on the surface with increased hydrophobicity instantly rolled off from an inclined plane, taking away graphite particles. This demonstrates the "lotus effect" on the modified teflon surface.

Also, the self-cleaning process was carried out by dipping the plates graphite shavings in the water. After several dipping cycles, the initial teflon surface remained dirty, while the modified surface was cleaned due to its superhydrophobic properties (Fig. 6).

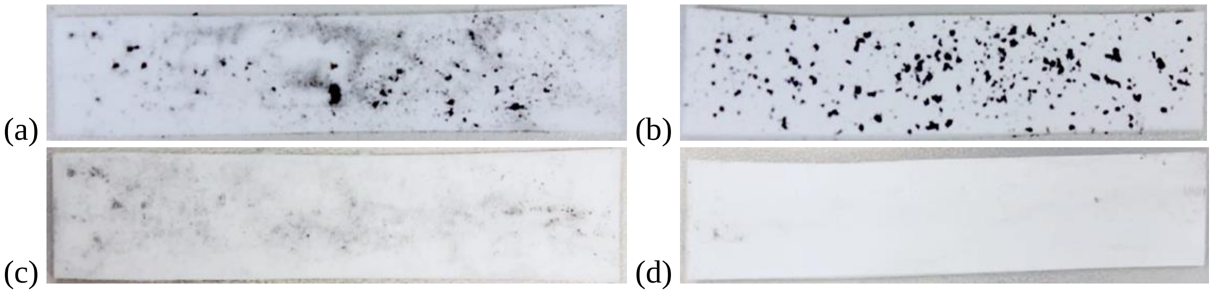

Figure 6. Optical images of (a) initial and (b) modified teflon surfaces contaminated with graphite particles; (c) initial and (d) modified surfaces after dipping into the water.

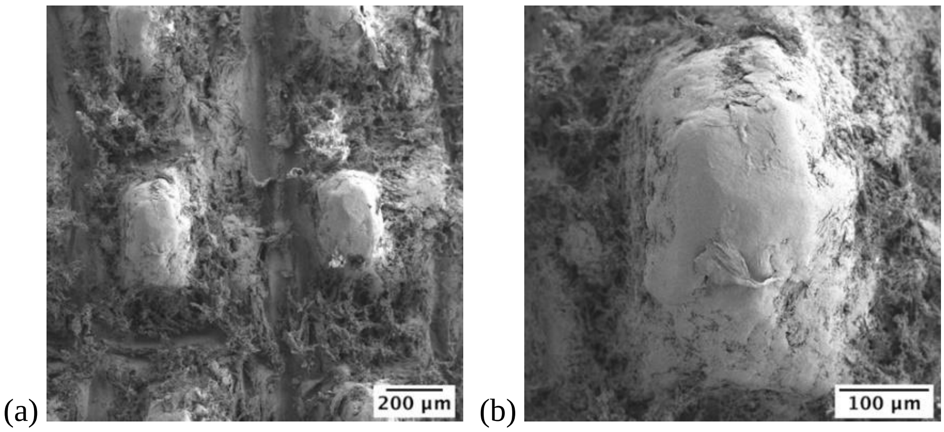

Figure 7. SEM images of the two-dimensional structure on teflon surface: (a) an array of hills; (b) the individual hill.

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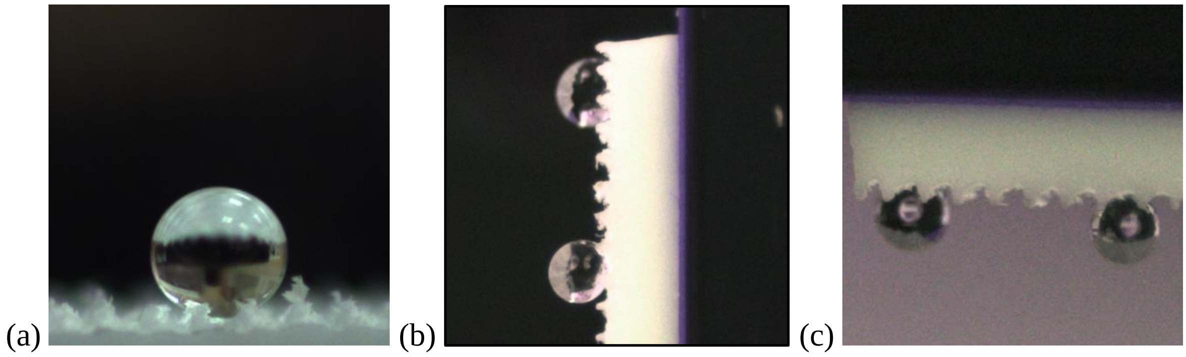

Figure 8. Water droplets placed on the highly adhesive superhydrophobic surface: (a) horizontal surface; (b) surface tilted on 90°; (c) surface tilted on 180°. Droplet volume (a) 6 μL, (b,c) 3 μL.

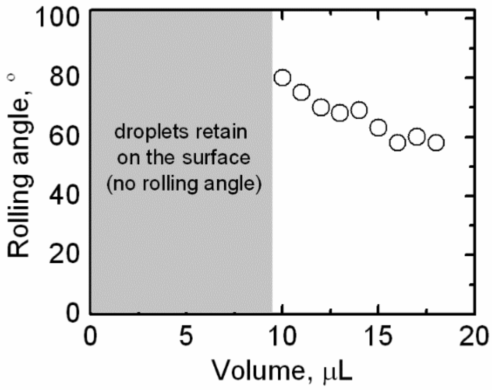

Figure 9. Dependency of the rolling angle on the droplet volume for teflon surfaces with two-dimensional structure.

3.5. Rose petal effect

It was shown that the samples with two-dimensional structures on the surface demonstrated super adhesive properties – "rose petal effect". The structures consisting of hills were produced by laser scanning and subsequent mechanical removal of the formed fibrous layer. SEM imaging showed that the produced hills had a pyramidal shape with height about 500 μm, width about 205 μm, and length about 295 μm (Fig. 7). The period of the structure was 500 μm in one direction and 380 μm in another one.

It was revealed that the surfaces with two-dimensional structure were super-hydrophobic with the maximal value of the contact angle 154.5° in our research (Fig. 8a).

For the obtained highly adhesive superhydrophobic surface, the sliding (rolling) angles depended on the droplet volume. As in the case of rose petal effect, the surfaces held the droplets with volume up to 9 μL (Fig. 9). The maximal volume of the retained droplet was about 18 μL. The observed effects can be attributed to the surface relief of the two-dimensional structure. The further research will be done for detail explanation of the obtained results.

4. Conclusion

The teflon surface modification by nanosecond CO_2 laser treatment to improve hydrophobic properties to superhydrophobicity has been demonstrated. The modified teflon surfaces also have exhibited superoleophilic properties. It has been revealed that the modified teflon surfaces exhibit the self-cleaning properties or "lotus effect". The highest value of the contact angle

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(θ = 154.5°) has been obtained for a sample with two-dimensional structures created using two-stage surface treatment: structure formation by CO_2 laser and mechanical removal of the fibrous layer. Such two-dimensional structures with morphology similar to rose petal have demonstrated super adhesive properties ("rose petal effect"), which allowed retaining water droplets with volume up to 18 μL.

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